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2.	Patent application number *(The Patent Office will fill in this part)*	9920871.2 -6 SEP 1999
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	IMPERIAL CHEMICAL INDUSTRIES PLC IMPERIAL CHEMICAL HOUSE MILLBANK LONDON SW1P 3JF
	Patents ADP number *(if you know it)*	935003
	If the applicant is a corporate body, give the country/state of its incorporation	UNITED KINGDOM
4.	Title of the invention	CATALYSTS
5.	Name of your agent *(if you have one)* "Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	~~CHRISTOPHER GRATWICK ICI GROUP INTELLECTUAL PROPERTY PO BOX 90 WILTON MIDDLESBROUGH CLEVELAND TS90 8JE ENGLAND~~ Christopher Gratwick Synetix Intellectual Property Department P.O. Box 1, Belasis Avenue Billingham Cleveland TS23 1LB
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Continuation sheets of this form	
Description	6
Claim(s)	2
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8

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11. I/We request the grant of a patent on the basis of this application.

Signature

Date 3 September 19

12. Name and daytime telephone number of person to contact in the United Kingdom

CHRISTOPHER GRATWICK
(01642) 432710

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Catalysts

This invention relates to catalysts and in particular to copper catalysts.

Copper catalysts are often employed for reactions involving hydrogen, for example simple hydrogenation reactions and for methanol synthesis (where carbon oxides are reacted with hydrogen), methanol decomposition (where methanol, often in admixture with steam, is decomposed to form hydrogen and carbon oxides) and the shift reaction (where carbon monoxide is reacted with steam to produce hydrogen and carbon dioxide) and the reverse shift reaction. Often, in order to obtain the optimum activity and stability of the catalyst, the catalyst is made with the copper in a highly dispersed form, for example by precipitation of a copper compound in the presence of, or together with, one or more support materials, especially zinc, magnesium, chromium and/or aluminium compounds. Following such precipitation, the composition is heated to convert the copper, and, if necessary also support materials, to the corresponding oxides. Prior to use for the desired reaction, the copper oxide is reduced to metallic copper. Particularly suitable catalysts for the above reactions are copper/zinc oxide/alumina and copper/zinc oxide/chromia compositions. In some cases part of the zinc may be replaced by magnesium and/or part of the alumina or chromia may be replaced by ceria or a rare earth such as lanthana.

The copper catalysts are readily de-activated by the presence of chlorine compounds, such as hydrogen chloride, in the process gas undergoing the reaction. Traces of such chlorine compounds may arise from contaminants in the materials, for example hydrocarbon feedstock, steam, air, employed to make the process gas. Such chlorine compounds react with the active copper forming copper chloride. Since copper chloride is relatively low melting, at the temperatures at which the catalysts are commonly employed, e.g. 150-300°C, the copper is mobilised and tends to aggregate resulting in a loss of dispersion of the copper and consequent loss of activity of the catalyst. Also where zinc and/or magnesium oxide is a component of the catalyst, likewise the corresponding chlorides may be formed, and these likewise are liable to be mobilised resulting in loss of the stabilising effect of the zinc or magnesium oxides, again with the consequent loss of dispersion and activity of the copper.

In order to overcome this problem it has been proposed in GB 1 357 335 to provide a guard bed upstream of a copper shift catalyst, the guard bed comprising solid particles of, or containing, a material that is more basic than zinc oxide. Examples of guard beds proposed are oxides of alkali metals, alkaline earth metals, manganese, yttrium or lanthanum, supported on alumina particles. It is also known to use part of the copper-containing catalyst as a sacrificial guard bed.

However, where the process gas contains steam, as in the case of the aforesaid shift and methanol decomposition reactions, there is a risk that under certain conditions, e.g. plant upsets, water will condense on the guard bed and/or catalyst. In such circumstances chlorides

formed by reaction of the basic material in the guard bed with the chlorine contaminants of the process gas may be washed out of the guard bed into the catalyst, again giving a loss of dispersion and activity of the catalyst.

We have found an alternative guard bed material that minimises such risk of de-activation of the catalyst.

Accordingly we provide a combination comprising a bed of a particulate copper-containing catalyst and, upstream of the catalyst bed, a guard bed of a particulate composition containing a) lead and/or at least one lead compound selected from lead oxide and lead compounds that decompose to lead oxide upon heating and b) a support therefor.

The invention also provides a process wherein a process gas is subjected to a catalytic reaction using a bed of a copper-containing catalyst comprising passing the process gas through an guard bed as aforesaid prior to passage through the bed of the copper-containing catalyst.

In the present invention, lead and/or lead oxide and/or a lead compound that decomposes upon heating to lead oxide is employed in the guard bed. Suitable heat decomposable lead compounds include lead acetate, lead nitrate, basic lead nitrate, lead carbonate, basic lead carbonate and lead hydroxide. A guard bed containing a heat decomposable lead compound may be charged to the reactor in which the process is effected and the decomposition effected during operation, i.e. by passing the heated process gas through the bed. In some cases, where the process gas is of a reducing nature, the process conditions may be such that the lead oxide is reduced by the process gas to elemental lead.

The support may be particles of an inert material such as alumina, chromia, zirconia, titania, or, less preferably, silica. The support preferably has a relatively high surface area, e.g. above 50 m^2/g. In order to provide an adequate guard effect without the need for an excessive volume of guard bed particles, the guard bed particles preferably have a lead content of at least 2% by weight, more preferably at least 5% by weight, particularly at least 10% by weight, and most particularly at least 15% by weight. The guard bed particles may be made by impregnating preformed shaped particles, e.g. spheres or cylinders, of the support with a solution of a suitable lead salt, followed by heating to remove the water and optionally to decompose the lead salt to the oxidic form. Alternatively, the guard bed particles may be made by precipitating the lead compound in the presence of the support particles or by co-precipitating lead and support, or support precursor, compounds followed by heating as necessary and forming the precipitated compounds into shaped particles before or after such a heating step. The guard bed particles preferably have maximum and minimum dimensions in the range 1.5 to 20 mm, particularly 3 to 6 mm.

The guard bed and the catalyst bed are fixed beds and may be in the same vessel or in different vessels, with the guard bed upstream of the catalyst bed. Preferably the process gas

flows down through the catalyst bed: thus where the guard and catalyst beds are in the same vessel, the guard bed will be a layer of the guard bed particles on top of the catalyst bed particles. If desired there may be a layer of an inert material between the guard bed and the catalyst bed to facilitate replenishment of the guard bed without disturbing the catalyst bed.

The invention is of particular utility in relation to the shift reaction. In this process a process gas stream containing carbon monoxide and steam, and often other components such as hydrogen, carbon dioxide, methane, and/or nitrogen, is passed through a bed of the copper-containing catalyst, especially a copper/zinc oxide/alumina or copper/zinc oxide/chromia catalyst in which some of the zinc oxide may be replaced by magnesia and/or some of the alumina and/or chromia may be replaced by a rare earth, at a temperature in the range 150 to 300°C, especially at an inlet temperature in the range 150 to 250°C. The process gas preferably contains 1 to 4% by volume of carbon monoxide, and at least one mole of steam per mole of carbon monoxide. Preferably the process gas contains 20 to 50% by volume of steam. Typically the process is operated at a wet gas space velocity in the range 2000 to 5000 h^{-1}, and at a pressure in the range 10 to 50 bar abs.

The invention is illustrated by the following examples. In the examples, various guard beds were tested as follows. 0.393 ml (0.50 g) of particles of a standard copper oxide/zinc oxide/alumina low temperature shift catalyst precursor containing about 50% by weight of copper oxide and having a particle size in the range 0.6 – 1.0 mm was charged to a microreactor and a layer of particles of fused alumina (0.25 g) of particle size 0.6 – 1.0 mm was charged on top of the shift catalyst precursor. 0.197 ml of the guard material particles of particle size 0.6 – 1.0 mm were charged on top of the fused alumina particles to give a total catalyst bed of volume of 0.70 ml.

The copper oxide in the catalyst precursor was reduced to metallic copper by passing a stream of nitrogen containing 2% by volume of hydrogen down through the microreactor at a pressure of about 28 bar abs. at a flow rate of 15 litres/hour (at NTP) while the microreactor was heated from ambient temperature to 220°C and held at this temperature for 95 minutes to give a total reduction time of 3.5 hours.

The catalyst activity for the water gas shift reaction was determined at a temperature of 220°C and a pressure of about 28 bar abs. using a gas mixture comprising 1 part by volume of steam to 2 parts by volume of a gas of volume composition H_2 55%, CO_2 15%, CO 5%, and N_2 25% at a total flow rate of 50 litres/hour.

To simulate chloride contamination, after the gas mixture had been passed through the catalyst bed for about 6 hours, HCl was added to the gas mixture to give an HCl concentration in the wet gas of 5.2 ppm by volume (test series A) and 1 ppm by volume (test series B). Under these fixed test conditions, the variation of CO conversion with time on line was

measured using in-line infra-red detection. A decrease in CO conversion with time is indicative of loss of activity of the catalyst.

Example 1

30 g of gamma alumina particles of size 0.6 – 1.0 mm and having a BET surface area of 350 m^2/g was dipped in 200 ml of an aqueous solution of lead(II) nitrate at 60 to 70°C and of approximate concentration 6.8 g of lead(II) nitrate per 100 ml of solution. The material was removed from the solution after 20 minutes, drained, dried at 110°C for two hours and then calcined in an oven at 300°C for two hours. Analysis of the resultant material showed a lead content of 6.4% by weight.

Example 2

Example 1 was repeated but using an aqueous solution containing 20.3 g of $Pb(NO_3)_2$ per 100 ml of solution. Chemical analysis of the resultant product showed a lead content of 10.7% by weight.

Example 3

Example 1 was repeated but using an aqueous solution of approximate concentration 37 g of $Pb(NO_3)_2$ per 100 ml of solution. After calcination of the material at 300°C, the sample was re-dipped using a second aqueous solution containing about 37 g of $Pb(NO_3)_2$ per 100 ml of solution and then drained, dried at 110°C for two hours and then calcined in an oven at 300°C for two hours. Chemical analysis of this material gave a lead content of 19.9% by weight.

Example 4

A 1.5 M solution of Na_2CO_3 and 5 litres of a solution containing 1843 g of $Al(NO_3)_3.9H_2O$ and 15.05 g of $Pb(NO_3)_2$ were heated to 80°C and added to 1 litre of demineralised water at a temperature of 70°C and at rates sufficient to maintain a pH of approximately 6.8. The resultant slurry was aged at 70°C for 30 minutes, washed and filtered and then dried at 110°C for 16 hours. The dried sample was then calcined in an oven at 300°C for 6 hours, 2% graphite by weight was added and the resultant product formed into pellets of size 0.6 – 1.0 mm. The product had a lead content of 3.5% by weight. Despite the washing step the product had a residual sodium content of about 1.1% by weight.

Samples of the guard bed materials were tested as described above. For purposes of comparison, in Comp A, the guard bed was 0.197 ml of the untreated gamma alumina particles as used for making the guard materials of Examples 1 to 3, and in Comp B the guard bed was 0.197 ml of the catalyst particles. For test series A, the % CO conversion was determined for a period of over 5 days with measurements being taken at intervals of about 2-3 hours (about 6-7 hours for the guard bed material of Example 4). For test series B, measurements were taken about every 6 hours over a period of 11 days. To assist comparison, the CO conversion measurements were plotted against time-on-line and a smooth curve drawn through the points

for each Example. (The individual points showed little variance from the smooth curves). From these plots, the conversion at regular intervals (every 6 hours for test series A and every 24 hours for test series B) was determined and are shown in the following tables wherein the % CO conversion figures have been rounded to the nearest integer.

Table – Test Series A

Time on line (hours)	CO conversion (%)					
	Ex 1	Ex 2	Ex 3	Ex 4	Comp A	Comp B
6	92	92	92	92	92	95
12	90	91	91	90	92	94
18	90	90	90	89	90	92
24	89	90	89	89	85	90
30	84	88	88	88	76	87
36	78	85	87	88	66	83
42	70	80	86	87	50	78
48	61	72	86	85	27	70
54	47	62	85	81	4	57
60	29	47	84	76	1	40

It is seen from the table that the guard bed materials of the invention have a similar effectiveness up to a time on line of about 30 hours, with the guard bed of Example 1 being somewhat inferior, presumably as a result of its relatively low lead content. In this regard it is calculated that the amount of hydrogen chloride fed to the guard bed in 30 hours is approximately the amount required to convert all the lead in the guard bed of Example 2 to lead(II) chloride. The alumina guard bed, Comp A, is initially as effective as the guard beds of the invention, presumably as a result of the reaction of hydrogen chloride with surface hydroxyl groups. However its performance rapidly deteriorates indicating that it has only a limited chloride capacity. The use of a sacrificial bed of catalyst as the guard bed, i.e. as in Comp B, initially gives a superior performance to the guard beds of the invention as a result of the

additional catalyst being available to catalyse the shift reaction (which is here operated under such a high space velocity that the reaction is activity rather than equilibrium limited - under the operating conditions, the carbon monoxide conversion required to reach equilibrium would be over 99%). However Comp B shows that the performance of the catalyst rapidly falls off, albeit not so fast as using untreated alumina as the guard bed.

Table – Test Series B

Time on line (hours)	CO conversion (%)			
	Ex 2	Ex 3	Comp A	Comp B
24	87	87	85	91
48	85	85	78	86
72	83	83	62	77
96	82	82	26	55
120	75	80	3	17
144	60	79	0	0
168	29	78	0	0
192	4	76	0	0
216	0	75	0	0
240	0	72	0	0

Calculation shows that for Examples 2 and 3 in test series B, significant de-activation commences when the total amount of HCl fed is equivalent to conversion of about 75% and 95% respectively of the lead to lead chloride. Again the lead containing guard beds were more effective in guarding against de-activation than the use of a sacrificial bed of the catalyst.

Claims.

1. A combination comprising a bed of a particulate copper-containing catalyst and, upstream of the catalyst bed, a guard bed of a particulate composition containing a) lead and/or at least one lead compound selected from lead oxide and lead compounds that decompose to lead oxide upon heating and b) a support therefor.

2. A combination according to claim 1 wherein the copper-containing catalyst is a copper/zinc oxide/alumina or copper/zinc oxide/chromia catalyst in which part of the zinc oxide may be replaced by magnesia and/or part of the alumina or chromia may be replaced by a rare earth.

3. A combination according to claim 1 or claim 2 wherein the particles of the guard bed have maximum and minimum dimensions in the range 1 to 20 mm.

4. A combination according to any one of claims 1 to 3 wherein the support is selected from alumina, chromia, zirconia and titania.

5. A combination according to any one of claims 1 to 4 wherein the guard bed particles contain at least 2% by weight of lead.

6. A combination according to any one of claims 1 to 5 wherein the guard bed particles are made by impregnating preformed shaped particles of the support with a solution of a suitable lead salt, followed by heating to remove the water and optionally to decompose the lead salt to the oxidic form.

7. A combination according to any one of claims 1 to 5 wherein the guard bed particles are made by precipitating the lead compound in the presence of the support particles or by co-precipitating lead and support, or support precursor, compounds followed by heating as necessary and forming the precipitated compounds into shaped particles before or after such a heating step.

8. A catalytic reaction using a bed of a copper-containing catalyst comprising passing the process gas through an guard bed of a particulate composition containing a) lead and/or at least one lead compound selected from lead oxide and lead compounds that decompose to lead oxide upon heating and b) a support therefor, prior to passage through the bed of copper-containing catalyst.

9. A process according to claim 8 wherein the process gas contains carbon monoxide and steam, and optionally hydrogen, carbon dioxide, methane, and/or nitrogen.

10. A process according to claim 9 wherein the process gas is passed through the copper-containing bed at an inlet temperature in the range 150 to 250°C.

11. A process according to claim 9 or claim 10 wherein the process gas contains 1 to 4% by volume of carbon monoxide, and at least one mole of steam per mole of carbon monoxide.

Abstract

A combination comprising a bed of a particulate copper-containing catalyst and, upstream of the catalyst bed, a guard bed of a particulate composition containing a) lead and/or at least one lead compound selected from lead oxide and lead compounds that decompose to lead oxide upon heating and b) a support therefor. The combination is of particular utility for the low temperature shift reaction wherein carbon monoxide is reacted with steam to produce hydrogen and carbon dioxide.